A Study on Microstructure, Mechanical and Oxidation Resistance Properties of HfMoNbTaTiZr-Base Refractory High-Entropy Alloys

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論文内容要約

※題名については，「要約」として下さい。

Chapter 1　Introduction

Over the last decade, high-entropy alloys (HEAs), which are expected to apply as the next generation of high-temperature materials, have been enormously studied due to their excellent performances. Among them, refractory high-entropy alloys (RHEAs) with high melting points show outstanding strength, especially at the high temperatures. However, the ductility at room temperature (RT) and oxidation resistance also need to be improved. Meanwhile, phase transformations in RHEAs are complex, and it is significant to be revealed.

Chapter 2　Alloy Design and Experimental Procedures

In this study, six elements of Hf, Mo, Nb, Ta, Ti and Zr are selected to prepare four different equimolar RHEAs. Hf, Mo, Nb and Ta are selected for SSS and high temperature softening resistance and a relatively lower density. Ti and Zr are mainly for decreasing density and maintaining a relatively high melting point. In addition, cause the small difference of melting points among these elements, slight segregation is expected to obtain in the eventual microstructure. Therefore, HfMoNbTaTiZr-base RHEAs in four different equimolar composition of 1# HfMoNbTaTi, 2# HfMoTaTiZr, 3# HfNbTaTiZr and 4# HfMoNbTaTiZr were fabricated by arc melting.

Chapter 3　Microstructure and Mechanical Property Studies on Four RHEAs

Four different equimolar RHEA Ingots with equiaxed grains microstructure were obtained by arc melting directly. All of them showed a body-centered cubic (BCC) matrix with different segregations and precipitates. Two critical parameters of δT_m (elemental melting point difference) and K_{alloy} (overall segregation coefficient in one alloy) were first proposed and established, which successfully explained the exponential relationship among RHEAs and Al-contained RHEAs. The new parameters can be applied to future alloy design and segregation estimating. All four RHEAs show high strength at 1200 °C and high hardness at RT, attributed to the dominant contribution of solid solution strengthening (SSS). After being homogenized in the condition of 1450 °C ×168 h, microstructures inclined to be decomposed and the yield strength was enhanced with a decrease of ductility. By introducing a binary model of $(MoNbTa)_x(HfTiZr)_y$, observations suggested that too much HCP elements addition, especially the Zr, will bring about more phase instability in these RHEAs. Considering the overall properties and phase stability, as-cast is a better condition for these RHEAs.

Chapter 4 Strengthening Mechanisms of 1# HfMoNbTaTi and the Homogeneous Nanoprecipitates

In particular, 1# HfMoNbTaTi in as-cast condition shows outstanding compressive performance and specific yield strength (1713 MPa with the ductility of 12% at RT). Meanwhile, it shows the highest yield strength of 851 MPa at 1200 °C, even compared with reported data. In addition, this alloy shows high phase stability even homogenized with 1450 °C ×168 h or compressed at 1200 °C. The as-cast microstructure was identified to consist of 3 phases: BCC matrix (a=3.3045 Å), monoclinic HfO_2 particles distributed along and close to the grain boundary. Additionally, another homogeneous disordered FCC nano-precipitates (a=4.5755 Å), primarily composed of Hf and Ti, was studied by STEM. Meanwhile, A semi-coherent interface with close mismatch was characterized between the matrix $(0,1,-1)_M$ and the precipitate $(0,2,0)_P$, and it showed high stability even after compressing at 1200 °C. Such a fine dense dispersed refractory precipitate is first obtained and characterized in as reported RHEAs. Strengthening mechanisms at RT in HfMoNbTaTi alloy are theoretically studied. SSS dominantly contributes 65% to its yield strength (1117 MPa). GBS also provides a visible 8% (132 MPa) proportion. In addition, nanoprecipitates contribute a non-ignorable increment of 367 MPa (21%) by the particle shearing mode based on observations, which is the first calculation in RHEAs fields. 1# HfMoNbTaTi alloy shows a high potential application in high-temperature fields.

Chapter 5 Microstructure Evolution and Mechanical Properties of HfNbTaTiZr

Mechanical properties and microstructure evolution at several annealing conditions of 3# HfNbTaTiZr were investigated in this chapter. In as-cast condition, microstructure consists of BCC matrix and nano-precipitate, which gives a high yield strength (1597 MPa) and a good ductility (no fracture evidence up to a strain of 50%). In addition, as-cast alloy has a high strength (356 MPa) at 1200 °C, which is almost four times of that in reported data. The significant enhancement may attribute to the nano-precipitation strengthening. After annealing at 1000 °C, HCP-1 phase forms which is composed of Hf, Zr, and a small amount of Ti, and it gradually dissolves as the temperature increases up to 1200 °C. When the temperature increases up to 1400 °C, HCP-1 phase entirely disappears and fine nano-precipitates form. The microstructure after annealed at 1450 °C for 168 h shows a phase decomposition. With the generation of two FCC phases and HCP-2 phase in the grain and on the grain boundary, nano-precipitates partly remains in the BCC matrix.

Chapter 6 Effect of Al on Microstructure and Oxidation Resistance Property of HfMoNbTaTi

Al significantly improves oxidation resistance. However, effective dense Al_2O_3 layer is easy to be destroyed due to the different thermal expansion. Besides, Al also enhances the hardness for the stronger bond formation with transition metals.

Chapter 7 Conclusions

It is important to point out that the homogeneous refractory nanoprecipitates with same morphology were obtained both in 1# HfMoNbTaTi and 4# HfMoNbTaTiZr. Furthermore, another similar fine and dense precipitates were also obtained in 3# RHEA, which also significantly improved the famous HfNbTaTiZr alloy in this work. These homogeneous precipitate in as-cast condition were first obtained and studied herein in RHEA fields. On the other hand, homogeneous nucleation mechanism (studied in 1# alloy) was assumed on account of the constituent fluctuation and point defects in the disordered matrix, and growth impeding was benefited from the observed lattice distortion, sluggish diffusion, and high cooling rate as well. And it is different from the conventional precipitate γ' in superalloys and Al-containing HEAs. Nucleation and growing mechanism are of great significance on HEA's further study. Meanwhile, the refractory nanoprecipitates, with high heat resistance and considerable precipitation strengthening effect, show a potential improvement by introducing to the high temperature materials. The new RHEA of HfMoNbTaTi indicated tremendous potential in high temperature applications. Meanwhile, nucleation and growth mechanisms of such finely dispersed refractory precipitates obtained in as-cast condition should be revealed and make it controllable and applicable in future alloys.